EFFECT OF TYPE OF SOLVENTS ON ASYMMETRIC POLYETHERSULFONE (PES) MEMBRANE FOR CO_2/CH_4 SEPARATION.

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ABSTRACT

This study investigates the influences of solvent on the structure and performances of polyethersulfone asymmetric flat sheet membrane for gas separation. The asymmetric flat sheet membrane were prepared by dry/wet phase inversion process consisting polyethersulfone (PES) as polymer, distillate water as a non-solvent and different solvent type was also added either dimethylformamide(DMF), dimethylacetamide (DMAc) or N-methyl-2-pyrrolidone (NMP). The dope formulated contains 20wt% polymer, 75wt% solvent and 5wt% non-solvent. Asymmetric flat sheet membranes were cast using a conventional casting technique. Methanol were used as the coagulation medium. The membranes are coated with 3wt% of polydimethylsiloxane (PDMS) mixed with 97wt% of n-hexane. The morphological structures of produced membranes were examined using Scanning Electron Microscope (SEM). The SEM images exhibited the best morphological structure was discovered from the membrane produced by using NMP as solvent followed by DMAc and lastly DMF. The Fourier Transform Infrared Spectroscopy (FTIR) analysis also conducted in order to detect the existence of the functional groups in the membrane. The performance of the membrane was examined by conducting the gas permeation test. Pure carbon dioxide (CO_2) and pure methane (CH_4) were used as the test gases by using feed pressure range from 1 to 3 bar. As predicted by the morphological structure, NMP solvent-membrane showed the best performance compared to DMAc solvent-membrane and DMF solvent-membrane. The selectivity of CO_2/CH_4 was 1.1358 (at 1 bar), 1.9946 (at 2 bar) and 2.6906 (at 3 bar) for NMP solvent-membrane, 1.0564 (at 1 bar), 1.8974 (at 2 bar) and 1.8958 (at 3 bar) for DMAc solvent-membrane and 0.9141 (at 1 bar), 1.7759 (at 2 bar) and 1.5257 (at 3 bar) for DMF solvent-membrane. Hence, solvent was discovered to affect the morphological structure which will consequently affect the performance of the polyethersulfone asymmetric flat sheet membrane. So, from the study conducted on solvent type, the most suitable solvent to produced high performance polyethersulfone asymmetric flat sheet membrane is NMP.

ABSTRAK

Kajian ini mengkaji pengaruh pelarut terhadap struktur dan prestasi membrane asimetrik lembar polietersulfon datar untuk pemisahan gas. Membran asimetrik lembar datar disediakan melalui teknik kering / basah inversi fasa proses yang mengandungi polietersulfon (PES) sebagai polimer, air suling sebagai jenis non-pelarut dan pelarut berbeza juga ditambah samada dimetilformamida (DMF), dimetil asetamida (DMAc) atau N-metil-2-pirolidon (NMP). Dop formula tersebut mengandungi polimer 20wt%, 75wt% pelarut dan% 5wt non-pelarut. Membran asimetris lembaran datar yang dijadikan menggunakan teknik casting konvensional. Methanol digunakan sebagai medium koagulasi. Membran tersebut dilapisi dengan 3wt% dari polydimethylsiloxane (PDMS) dicampur dengan 97wt% n-heksana. Struktur morfologi membran yang dihasilkan telah diuji dengan menggunakan pengimbas mikroskop electron (SEM). Imej SEM menunjukkan gambar struktur morfologi terbaik yang ditemui di membran yang dihasilkan dengan menggunakan NMP sebagai pelarut diikuti oleh DMAc dan terakhir DMF . Fourier Transform Spektroskopi Inframerah (FTIR) analisis juga dilakukan untuk mengesan kewujudan kumpulan berfungsi dalam membrane. Prestasi membran diperiksa dengan melakukan ujian permeasi gas. Karbon dioksida (CO_2) asli dan metana asli (CH_4) digunakan sebagai gas uji dengan menggunakan pelbagai tekanan dengan jarak dari 1 hingga 3 bar. Seperti yang diramal oleh struktur morfologi, NMP pelarut-membran menunjukkan prestasi terbaik berbanding dengan DMAc pelarut-membran dan DMF pelarut-membran dengan selektivitas CO_2/CH_4 adalah 1.1358 (pada 1 bar), 1.9946 (pada 2 bar) dan 2.6906 (pada 3 bar) untuk NMP pelarut-membran, 1.0564 (pada 1 bar), 1.8974 (pada 2 bar) dan 1.8958 (pada 3 bar) untuk DMAc pelarut-membran dan 0.9141 (pada 1 bar), 1.7759 (pada 2 bar) dan 1.5257 (pada 3 bar) untuk DMF solvent-membran. Oleh kerana itu, kesimpulannya pelarut mempengaruhi struktur morfologi yang secara lansung akan menjejaskan prestasi membran asimetrik lembar polietersulfon datar. Daripada kajian yang dilakukan pada jenis pelarut, pelarut yang paling sesuai untuk menghasilkan membrane asimetrik lembar polietersulfon datar berprestasi tinggi adalah NMP.

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LIST OF ABBREVIATIONS

CO_2	-	Carbon Dioxide
PES	-	Polyethersulfone
SEM	-	Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
RO	-	Reverse Osmosis
TIPS	-	Thermal Induced Phase Separation
H_2	-	Hydrogen
N_2	-	Nitrogen
CH_4	-	Methane
PSU	-	Polysulfone
P	-	Permeability
D	-	Diffusion Coefficient in Membrane
NMP	-	N-methyl-2-pyrrolidone
DMAc	-	Dimethylacetamide
DMF	-	Dimethylformamide
PDMS	-	Polydimethylsiloxane
P_i	-	Permeability for Gas component
Q	-	Gas Flowrate
A	-	Area
$\triangle P$	-	Pressure in System
Pj	-	Permeability of Another Gas Component
α	-	Selectivity

CSDS	-	Chemical Safety Data Sheet
IR	-	Infrared

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The separation of acid gases such as CO_2 and H_2S is of great importance in many industrial areas, such as upgrading of natural gas and greenhouse gas emission reduction. Since CO_2 reduces the energy content and is corrosive to the transportation and storage systems in the presence of water, CO_2 concentration needs to be reduced to less than 2% to reach the U.S. pipeline specification (Baker, 2002). On the other hand, the increasing public concern over global warming has concentrated on the greenhouse gas emission. It is highly desirable to remove and sequester CO_2 from various sources.

For natural gas sweetening, the most common process is amine absorption. However, amine plants are large and heavy, requiring tall structures which present problems for use on offshore platforms. They are very complex and require constant operator supervision and maintenance. Also, the presence of a generator which burns some of the methane is a fire safety hazard on offshore platforms. Compared to other technologies, membrane-based CO_2 capture has the advantages of low energy consumption, low weight and space requirement, simplicity of installation / operation, and high process flexibility. The extent of the benefits from using membrane technology is highly dependent on the nature of the separation problem. Natural gas is typically produced at high pressure which is deal for membrane separation. The carbon dioxide permeates through the membrane leaving a methane stream with essentially no pressure drop (Spillman *et al*, 1990). Membrane systems are extremely reliable since the process is continuous with few control components which can cause a shutdown.

In gas separation membrane process, the ability of a membrane to control the permeation rate of chemical species through it had made it favourable for separating mixture of gases. Preferably, membranes should exhibit high selectivity and high permeability simultaneously. However, current commercial membranes usually suffer for a trade-off between selectivity and permeability, which hinder the large-scale application in the industry.

1.2 Problem Statement

The key to high performance of membrane-based gas separation process is strongly depends on permeability and selectivity. Traditionally, there has been a trade-off between selectivity and permeability; where membrane with higher selectivity tends to exhibit less permeability and vice versa. Higher permeability of membrane will leads to higher productivity and lower capital cost while membrane with higher selectivity will shows more efficient separation process. One of the major problems confronting the use of membrane-based gas separation processes in a wide range of applications is the lack of membranes with high performance. Despite the limitation in achieving both high permeability and selectivity, it is important to select the most compatible combination of polymers and solvents formulation for flat asymmetric membrane that has improvement in the membrane properties for acid gas separation. Therefore, membrane formation process plays an important role and certain factors need proper attention in order to produce a good membrane for gas separation.

1.3 Objective of Research

The main objective of this study is to develop a high performance asymmetric flat sheet membrane for gas separation by study the effect of different solvents used in the formation of the membrane.

1.4 Scope of Research

Several scopes that have been outlined in order to achieve the objective of this study are as follows:

- To fabricate Polyethersulfone (PES) asymmetric membrane in flat sheet form by dry/wet phase inversion.
- To study the effect of different solvents used in the formation of asymmetric flat sheet membrane.
- To characterize the PES asymmetric flat sheet membrane using Scanning Electron Micrograph (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).
- To test the performance of the asymmetric flat sheet membrane in gas separation using single permeation test.

1.5 Rationale and Significant

- High performance membrane for gas separation (acid gas).
  - ✓ Flat asymmetric membrane exhibited greater gas selectivity than the dense membrane.

- Lower operating costs.
  - ✓ The only major operating cost for single-stage membrane system is membrane replacement. This cost is significantly lower than the solvent replacement and energy cost associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.

- Environmental friendly.
    - ✓ Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated.

- Good weight and space efficiency
    - ✓ Skid construction can be optimized to the space available and multiple elements can be inserted into tubes to increase packing density. This space efficiency is especially important for offshore environments.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane for Gas Separation

2.1.1 History of Membrane for Gas Separation

The history of membrane based gas separations can be traced back over 170 years. In 1829 Thomas Graham observed gaseous osmosis for the air-carbon-dioxide system through a wet animal bladder (Kesting and Fritzsche, 1993). Then, J. K. Mitchell in year 1831 observed that balloons made from India rubber put into gas atmospheres of different composition blew up with different velocities, depending on the nature of the gas (Baker, 1991). Mitchell noted that CO_2 was absorbed by rubber film to a larger degree than other gases, and was led to infer, accordingly, that rubber expanded in volume and hence, porosity was induced in the solid sample which provided a way of penetration of CO_2 molecules.

In 1855, Adolph Fick postulated the concept of diffusion and formulated Fick's First Law of diffusion from the studies on gas transport through nitrocellulose membrane (Baker, 1991). Of course, the significance of Fick's First Law is quite general for many scientific fields, but it is interesting that membranes were the media where it was first established.

Later in 1866, Graham discovered the Graham's law of gas diffusion. Graham's Law describe qualitative about "sorption diffusion" theory for gas transport or permeation through a membrane. In the experiments, gas permeated through the film (natural rubber) into vacuum not into air. Graham established a series of relative permeation rates across the film for a number of gases that is amazing lose to modern estimates of the corresponding properties then noted that there was no relation between these values and known diffusion coefficients in gases. Therefore, “solution diffusion” mechanism was proposed to describe the mechanism of gas permeate through the rubbery polymer.

Many other important findings in gas permeation research or membrane science more generally, can be attributed to Graham (Graham *et al*, 1866). Graham carried out the first membrane gas separation and obtained oxygen riched air containing 46.6% oxygen. By increasing the pressure of a gas mixture to be separated should be beneficial for obtaining higher fluxes. Graham observed that changes in the thickness of films affects the flux but not the composition of permeate gas. From the study, the effect of temperature on permeation rates is observed; by preparing the first composite membranes and tried to vary deliberately the chemical nature of the membrane material. Graham also described the experiments on hydrogen permeation across membranes made of platinum, palladium, and other metals and concluded that they as well as rubber films behaved like non-porous septa.

In 1891, Kayser demonstrated the validity of Hendry’ law for adsorption of carbon dioxide in natural rubber (Paul and Yampol’skii, 1994). In 1900, Lord Rayleigh measured relative permeabilities of oxygen, nitrogen and argon rubber. Other significant contributions in the understanding of membrane gas transport theory were made by Knudsen in 1908 (Knudsen diffusion defined) and Shakespear in 1917 through 1920 (temperature dependence of gas permeability in membranes). According to Dynes, the process of diffusion of a gas through a rubber film is determined by two more less separate processes. Measurement must be made simultaneously on the permeability, absorption coefficients, and diffusion-constants, as a minimum, any two of these three quantities (Rahman *et al*, 2006).

This method had been used since until in the 1930s and 1940s, R. M. Barrer widely introduced it to experimental practice, so it is often known as the Dynes-Barrer method. A great influence on our knowledge of the thermodynamics and diffusion properties of polymers was exerted by the introduction of McBain microbalances (Paul and Yampol’skii, 1994). This simple instrument made it possible to obtain abundant information, especially for polymer-vapor systems, on solubility coefficients, sorption isotherms, diffusion coefficients, and sorption kinetics.

2.1.2 Gas Separation System

There are four methods for gas separation in oil and gas industry which are cryogenics distillation, absorption, adsorption and membrane.

2.1.2.1 Cryogenics Distillation

Cryogenic distillation involves a series of vaporizations and condensations in which the higher boiling species concentrate in the liquid phase which flows down the column and the lower boiling components concentrate in the vapor phase which moves up the column. Heat is removed from the column at the top through a condenser while heat is added at the bottom of the column through the reboiler. Cryogenics is the predominant technology in the separation of atmospheric gases, methane from nitrogen, ethane and ethylene and is also used in hydrogen separations.

2.1.2.2 Absorption

Absorption is a physical process where a gas is selectively dissolved in a liquid and subsequently recovered through the action of heat, pressure, and/or another chemical. Absorption processes have found major applications in the removal of acid gases such as carbon dioxide and hydrogen sulphide (MacLean *et al*, 1986). The compensating advantage is that separation can often be effected at a more convenient temperature. Absorption comes into its own when the normal boiling points of the components are widely operated, or where one or more of the components have a strong affinity for a particular solvent. Hence its use with carbon dioxide removal from synthesis gas, and for scrubbing carbon dioxide and sulphur compounds from natural gas.

2.1.2.3 Adsorption

This technique uses a porous solid material such as a zeolite, an aluminosilicates material, or a carbon molecular sieve to preferentially adsorb one gaseous species versus others. The adsorbent is packed in carbon steel vessels and a higher pressure is used to adsorb while a lower pressure is used to desorb.

2.1.2.4 Membrane

Membrane which are thin barrier between feed and permeate gas streams have been used to selectively transport fluids since life itself. There have been however, the major technical advances that permit industrial use. The first was the research of Loeb and Sourirajan (1963) where thin asymmetric membranes consists of a thin, dense outside layer was formed on a thick, porous base layer, and were developed from cellulose acetate.This allowed high flux as well as good selectivity. This same principle has been applied to many other polymeric systems. Membranes have been formed into separators by either winding flat sheets into spirally wound modules or taking bundles of hollow fibers and casting epoxy resins on both ends and then encasing the bundle in carbon steel shells with appropriate entrance and exit nozzles (MacLean *et al*, 1986).

2.1.3 Comparison between Gas Separation Systems

Each of the four gas separation technologies are summarized with respect to their performance as shown in Table 2.1.Special attention will be given to product quality and general economic considerations.

Table 2.1: Comparison of Gas Separation Systems

Process	**Advantage**	**Disadvantage**
Cryogenic distillation	• Low power consumption • Could produce high purity products. • Could achieve higher recovery compared to other process.	• Unable to economically scale down to very small size. • Consist of highly integrated, enclosed system which does not permit easy handling of widely varying feed streams.
Adsorption	• Could obtain high purity of products. • Can be supplied to remote locations where equipment size is critical.	• Lower recovery of products. •Single relatively pure product.
Absorption	• Excellent for CO_2 and H_2S removal	• High partial pressure needed for physical solvents • Low partial pressure needed for chemical solvent slow purity of acid gas
Membrane	• Versatility • Simplicity • Stable at high pressure • Could achieve high purity of product.	• Possible recompression of permeate. • Medium purity.

2.1.4 Advantages of Membrane for Gas Separation

Membrane process is most favorable separating system since it combined several beneficial features that make them attractive for industrial applications. The features are described briefly below:

1) Separation is on basis of molecular size, which means that the separation process could be carry out at ambient or modest temperature. Thermally sensitive solutes can be treated without damage. Other environmental stresses, such as imposed by chemical additives and high shear can also be avoided or minimized (Baker, 2002).

2) Membrane separation process did not require any phase change and any latent heat. Thus, it could save lost of energy consumption (Baker, 2002).

3) Membrane devices are almost always compact and modular, especially if membrane is provided in a bundle of hollow fibers and spiral wound that occupies high area per unit volume (Spillman and Sherwin, 1990). This factor also leads towards weight and space efficiency, which is important in transportation or offshore platform applications.

4) Membrane process is environmental friendly because it produces no waste. In fact, one of the major accomplishments of membrane processes is that they provide a means for recovering value from previously discarded effluents (Baker, 2002).

5) Membrane devices could be easily scale up from pilot to commercial size, which allows pilot scale tests with a single module and then direct scale-up by simply using many multiples of this unit (Baker, 2002).

2.2 Membrane Classification

Typically, there are two types of membrane structure namely, symmetric and asymmetric. The different between these two structures were the physical and chemical properties.

2.2.1 Symmetrical Membrane

Symmetrical membranes have a uniform composition structure throughout, and they can be porous or dense. The resistance to mass transfer in these membranes are determined by the total membranes thickness. A decrease in membrane thickness results in an increased permeation rate (Strathmann, 1986).

2.2.1.1 Microporous Membrane

The simplest form of microporous membrane is a polymer film with cylindrical pores or capillaries. However, more commonly microporous membranes have a more open and random structure with interconnected pores. They are very similar in structure and function to conventional filters. However in contrast with conventional filters, these pores are extremely small (Strathmann, 1986).

2.2.1.2 Non-porous, Dense Membrane

This type of membranes consists of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rates within the membrane, which are determined by their diffusivity and solubility in the membrane material. Thus, this type of membranes can separate permeants of similar size if their concentration in the membrane material differ significantly (Strathmann, 1986).

2.2.1.3 Electrically-Charged Membranes

These types of membranes are also referred to as ion-exchange membranes. They can be dense or microporous, but most commonly are very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. Separation is achieved mainly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is affected by the charge and concentration of ions in the solution. This type of membranes is used for processing electrolyte solution in electrodialysis.

2.2.2 Asymmetric Membranes

Asymmetric membranes are used primarily for pressure driven membrane processes, such as ultrafiltration and gas separation. Their structure consist of a very thin (0.1 to 2.0μm) polymer layer on highly porous 100 to 200μm thick sublayer (Strathmann, 1986). This means that this membrane consist two layer; a thin, dense and nonporous skin layer that perform the separation, supported by on a finely microporous substrate that made from the same material that only provides the mechanical strength (Baker, 2002). The sublayer only acts as a support and does not affect the separation characteristics or the permeation rate of the membrane in pressure driven processes. To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin (Baker, 2002). Since the permeation rate in ultrafiltration or gas separation processes is inversely proportional to the thickness of the thin barrier layer, asymmetric membranes exhibit much higher permeation rates than symmetric structures of comparable thickness. Another advantage of asymmetric membranes is the membranes are surface filters retaining all the rejected materials at the surface where they can be removed by shear forces applied by the feed solution moving parallel to the membrane surface (Costello, 1994). Ideal asymmetric membrane for gas separation should meet the following requirement. (Paul and Yampol’skii, 1994).

1) The selective skin layer should defect free so that gas transport takes places exclusively by solution diffusion not by poorly selective flow through process.